BAT456

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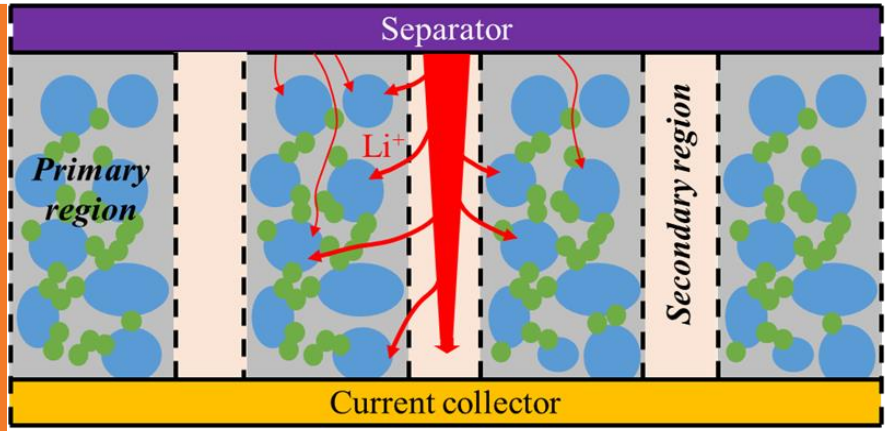
XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

ANODE STRUCTURES THAT ENHANCE FAST CHARGE



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Argonne NATIONAL LABORATORY | SLAC | NREL | BERKELEY LAB | INL Idaho National Laboratory | OAK RIDGE National Laboratory

June 2, 2020
Virtual Meeting due to COVID-19

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 75%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

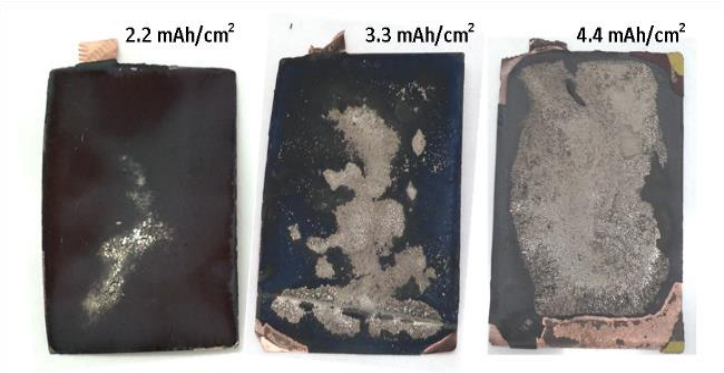
- Funding for FY20 – $5.6M

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab
- Oak Ridge National Lab

RELEVANCE

- Fast charging at rates over 2C can result in lithium plating on typical negative electrodes.
- Lithium plating is more likely with thicker electrodes and lower temperature.
- High tortuosity in the anode is also likely to favor lithium plating.
- Carefully selected design of experiments that include modeling, fabrication and testing of prototype cells, and post-test diagnostics are needed to develop a cell system that minimizes the possibility of lithium plating in EV batteries.



Gallagher, *et al., JES* 2016

OBJECTIVE

- The objective of the XCEL-Anode Thrust effort is to design and fabricate electrode architectures that minimize the possibility of lithium plating under fast charge conditions.

APPROACH

- Modeling team (NREL) will predict ideal anode and cathode architectures that prevent anode from going below lithium potentials, and determine effect on energy density. BatPaC Model (Argonne) will be used to estimate impact on cost.
- CAMP Facility (Argonne) and LBNL will fabricate electrodes that best approximate the electrode architectures predicted by modeling effort and assemble cells to validate electrochemical performance. Cells will be made with graphite vs. NMC electrodes with loadings between 2 and 4 mAh/cm^2. Latest advanced electrolytes (INL & NREL) will be utilized and compared to baseline.
- Post-Test Facility (Argonne) will post-mortem cells for presence of lithium plating.

MILESTONES

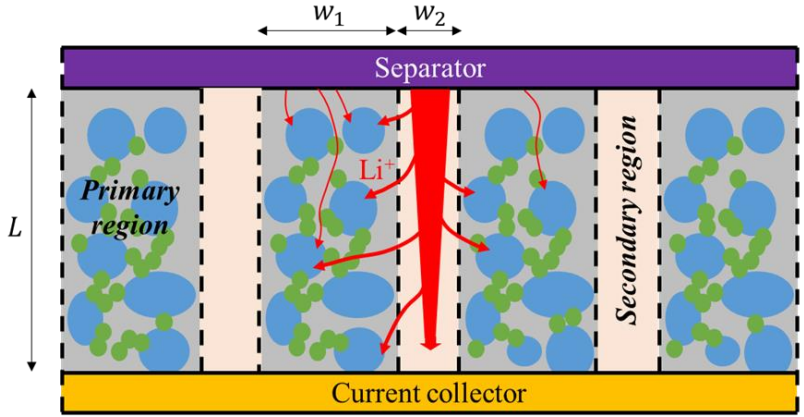
Related milestones in XCEL – Anode & Electrolyte Thrust

Milestone	End Date	Status
Identify & optimize best anode composition and architecture	6/30/2020	On-Track
Identify & optimize best electrolyte composition and accompanying formation process	6/30/2020	On-Track (See BAT471)
Fabricate 24 pouch cells using best anode and electrolyte	8/30/2020	May be delayed due to COVID-19
Estimate cost of fast charge designs using BatPaC	9/30/2020	On-Track

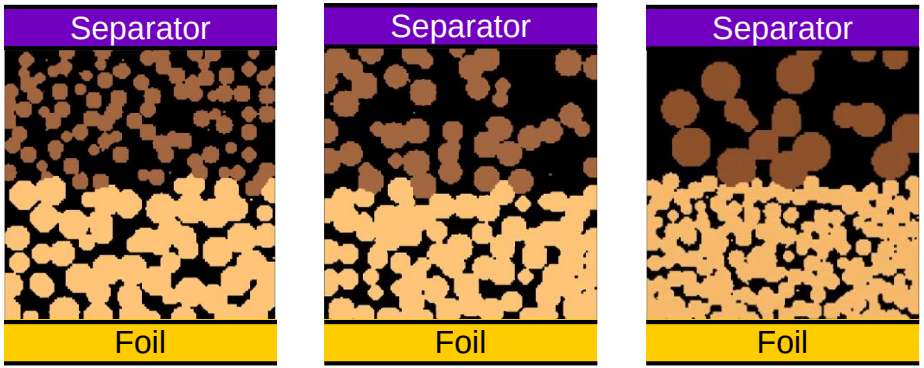
ELECTRODE ARCHITECTURES BEING STUDIED

Modeling predictions identified two major systems to consider:

- Secondary Pore Network (SPN)
  - Create ion pathways directly to back of electrode (near foil)

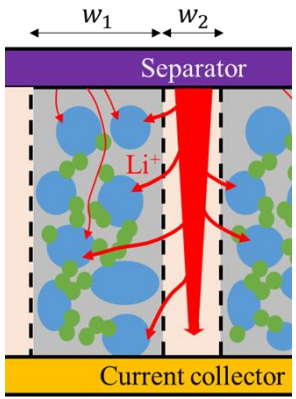


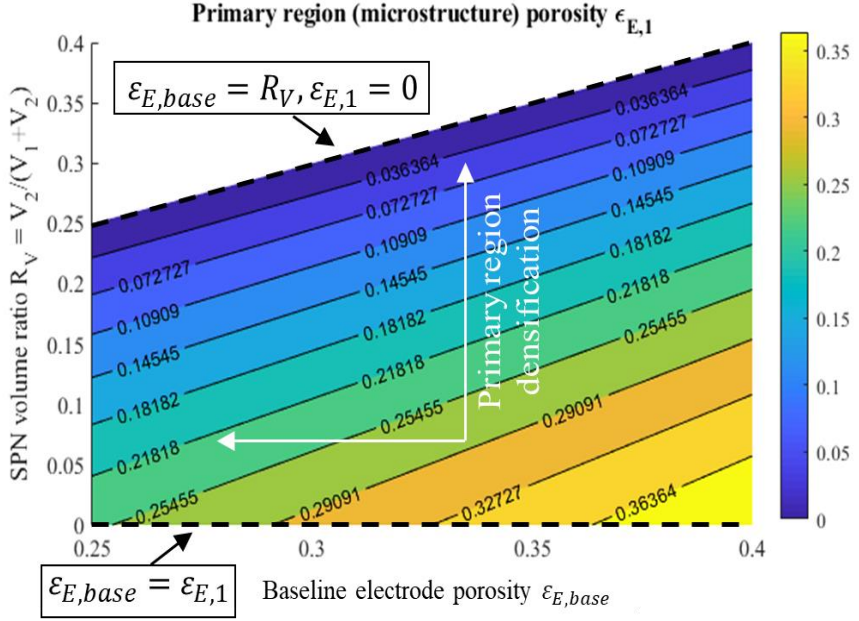
- Bilayer
  - Vary particle size and/or porosity of each layer



SECONDARY PORE NETWORK ELECTRODE ARCHITECTURE FOR FAST CHARGE

SPN improves through-plane diffusion but degrades in-plane diffusion within the primary region due to densification



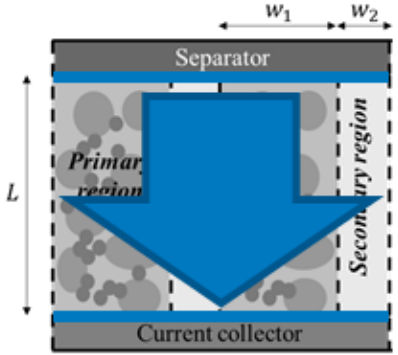


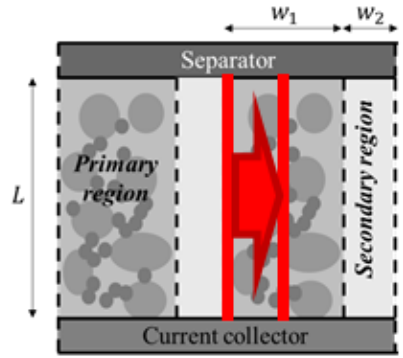
- To keep identical gravimetric- and volumetric-specific theoretical capacities with the baseline, the primary region must be densified to balance the additional pores
- Nonuniform in-plane utilization of the active material and potential electrolyte depletion/saturation in the center of the primary region is expected to reduce actual capacity and may trigger earlier degradation

F. L. E. Usseglio-Viretta et al., Electrochimica Acta 342(10) 136034, ***2020***

SPN DESIGN OBSERVATIONS & CRITERIA

Secondary pore network (SPN) architecture has a combined positive through-plane and negative in-plane diffusion impact





Characteristic diffusion time from separator to current collector:

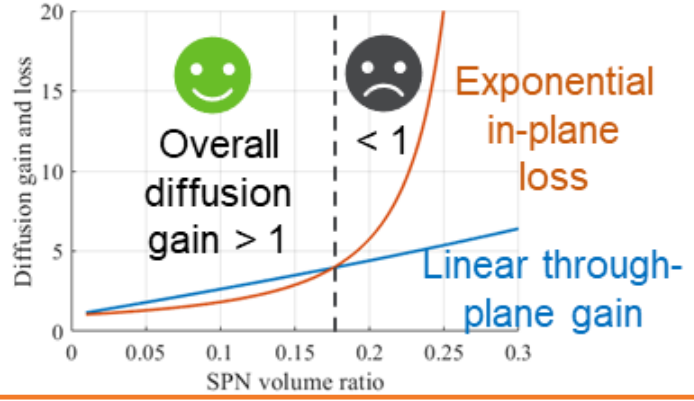
$$t_{tot}^{tp} = \frac{L^2}{D_{tot}^{tp}}$$

Characteristic diffusion time from primary region boundary to center

$$t_1^{ip} = \frac{{w_1}^2}{4D_1^{ip}}$$

$$\frac{t_{tot}^{tp}}{t_1^{ip}} = 1 \Rightarrow \frac{D_{tot}^{tp}}{D_1^{ip}} = \frac{4 \times L^2}{{w_1}^2}$$

The time for Li+ to diffuse to the inner primary region particle should be the same as the time for a Li+ to diffuse to the foil to guarantee equal utilization of all particles, and prevent Li plating on foil.



F. L. E. Usseglio-Viretta et al., Electrochimica Acta 342(10) 136034, ***2020***

SPN volume is limited by in-plane transport limitation
(optimal varies with electrode)

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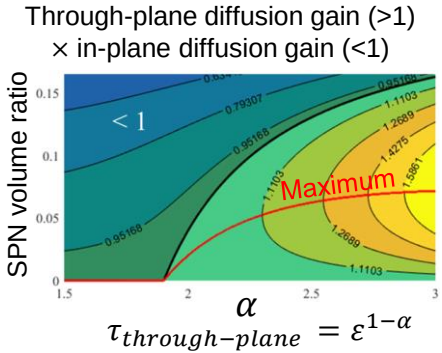
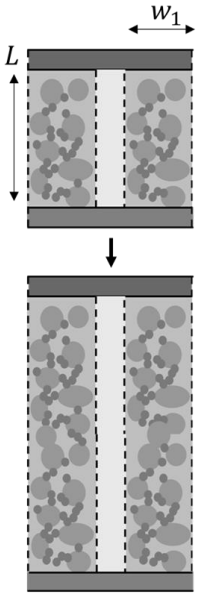
IDENTIFYING ELECTRODES MOST SUITED FOR SECONDARY PORE NETWORK ARCHITECTURE

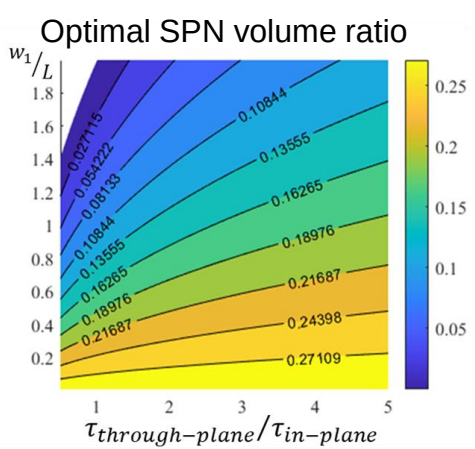
Anisotropic electrode materials is a good fit for SPN architecture

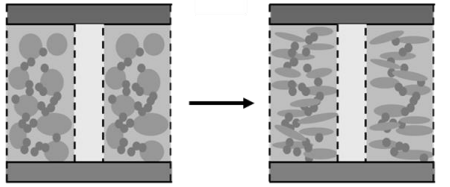
- SPN with anisotropic particles is a better fit than spherical particles: channels provide through-plane separator-to-current collector highways diffusion, while flake-like particles enhance in-plane diffusion limiting the negative impact of microstructure densification
- Elongated particles misaligned with the diffusing path (e.g., A12 graphite) are then a relevant application for SPN; while not recommended for baseline electrodes!
- Optimizing XFC electrodes would require accounting for cost tradeoffs between differences in raw materials for flake/spherical and added expense of SPN processing



(Top) Overall diffusion gain is higher for electrode with a baseline high through-plane tortuosity (e.g. graphite A12). Limited gain is achieved with electrodes that exhibit already a relatively low tortuosity (e.g. SLC1506T).







e.g. SLC1506T (~1.1-1.4)

e.g. A12 graphite (~2.5)

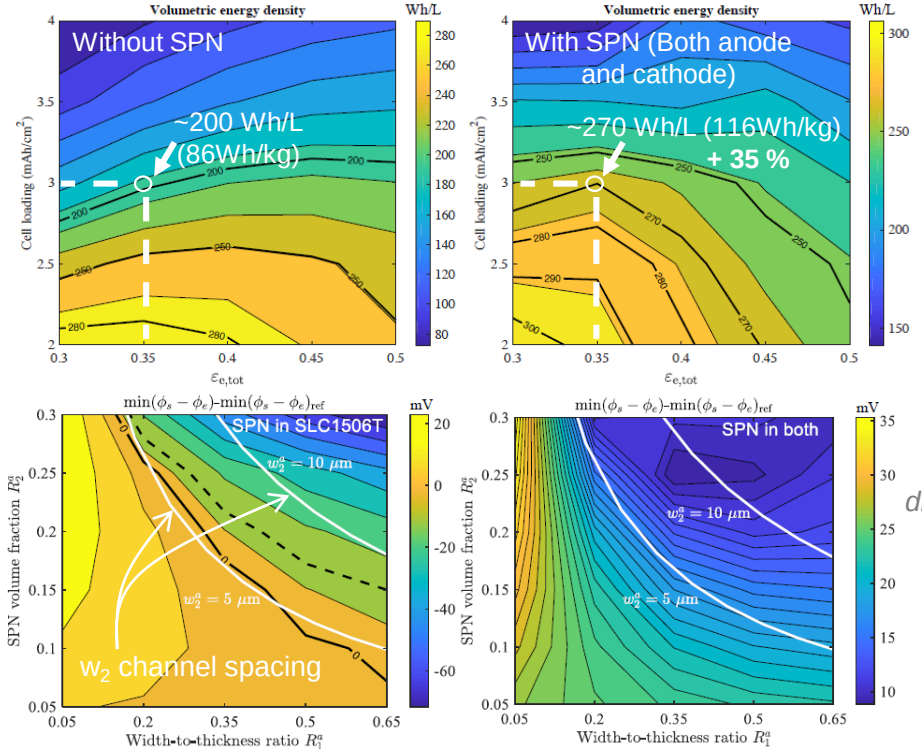
(Right) High through-plane tortuosity is often derived from tortuosity anisotropy due to particle misalignment, and allows increasing SPN volume

F. L. E. Usseglio-Viretta et al., Electrochimica Acta 342(10) 136034, ***2020***

PERFORMANCE IMPROVEMENTS GRANTED BY SECONDARY PORE NETWORK ARCHITECTURE

Anisotropic electrode materials is a good fit for SPN architecture

- Structured electrodes with SPN reached 116 Wh/kg (52% of theoretical energy density) after 6C CC and 173.9 Wh/kg (77%) after 10 minutes CC CV
- SPN reduces driving force for lithium plating. Manufacturing capabilities limit highest improvements.
- Highest improvement predicted when both anode and cathode have a SPN

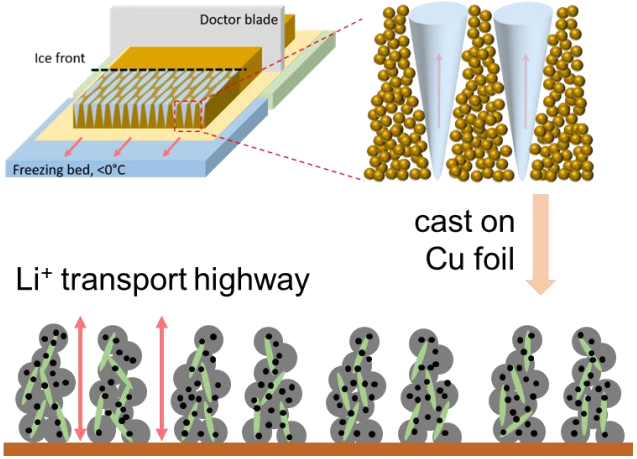


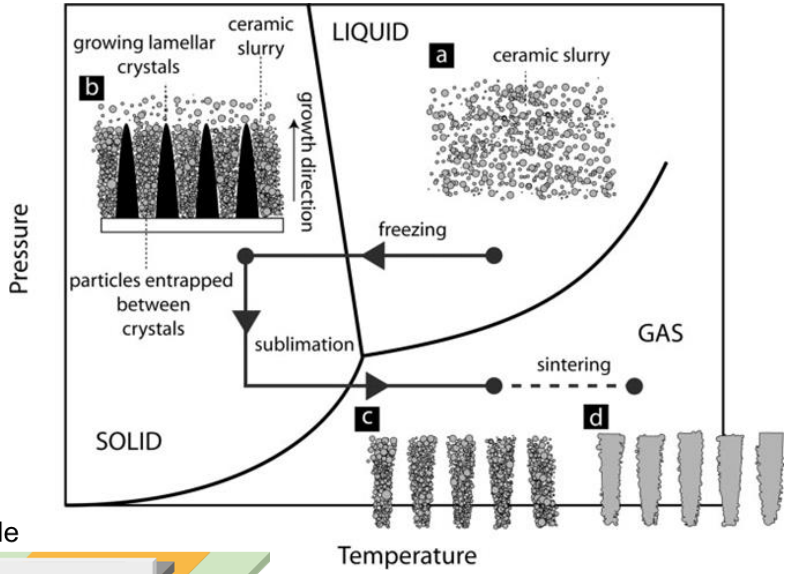
3 mAh/cm², 6C CC (cut off voltage 4.2V) @45°C with 8.4 µm channel spacing (w2), 3 µm channel width and 0.26 SPN volume ratio.

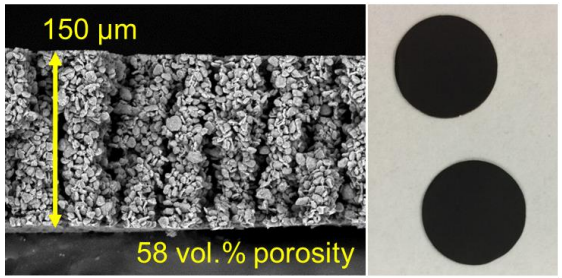
Potential for lithium plating difference between structured and baseline electrodes calculated at the end of a 6C charge.

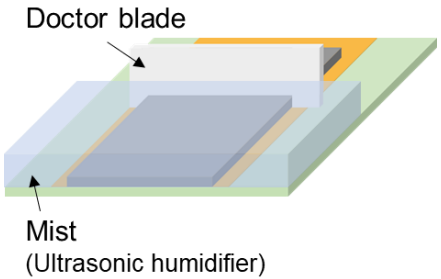
W. Mai et al., Electrochimica Acta 341(1) 136013, ***2020***

FABRICATE THE IDEAL SPN ELECTRODE VIA FREEZE-TAPE CAST METHOD









New setup developed to control thickness by doctor blade. Water evaporation suppressed by mist.

TAILOR FREEZE-TAPE CAST FOR GRAPHITE

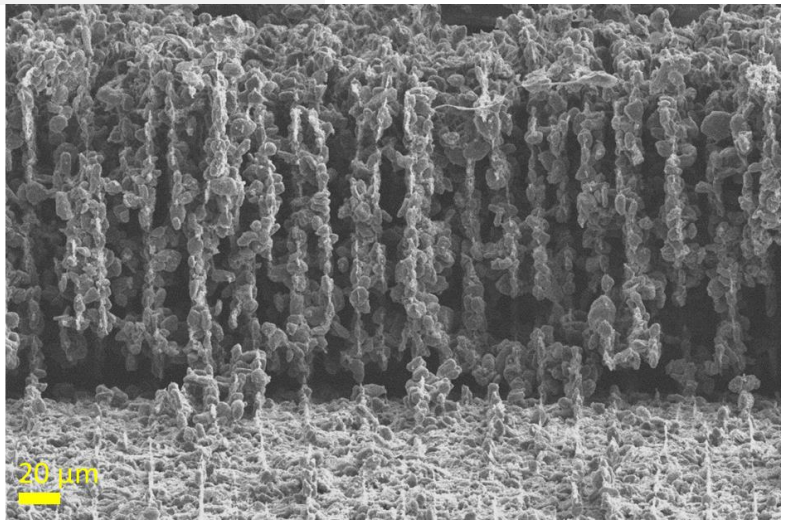
Freeze-Tape Cast Onto Thin Graphite Layer Improved Adhesion

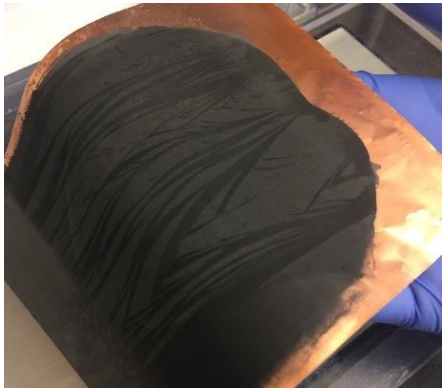
Tape cast

1506T/C45/**PVDF**/
Oxalic Acid
(91.8/1.9/6.1/0.2)

Freeze Tape cast

1506T/C45/**CMC/SBR**
(90/1.9/2.7/5.4)





- ↑ Two cast layers adhere well.
- ↑ Oriented pores in the freeze tape cast layer.
- ↑ Pores continue to surface.
- ↑ Good adhesion to Cu foil.

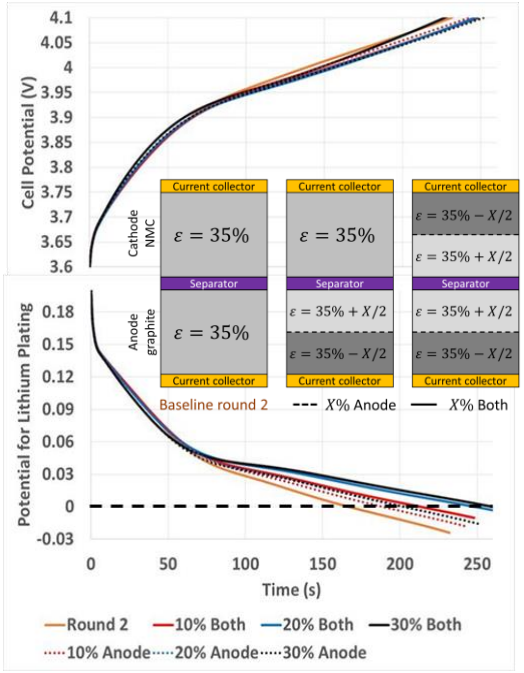
- Efforts are now focused on lowering porosity

DUAL LAYER ELECTRODE ARCHITECTURE FOR FAST CHARGE FOR ANODE & CATHODE

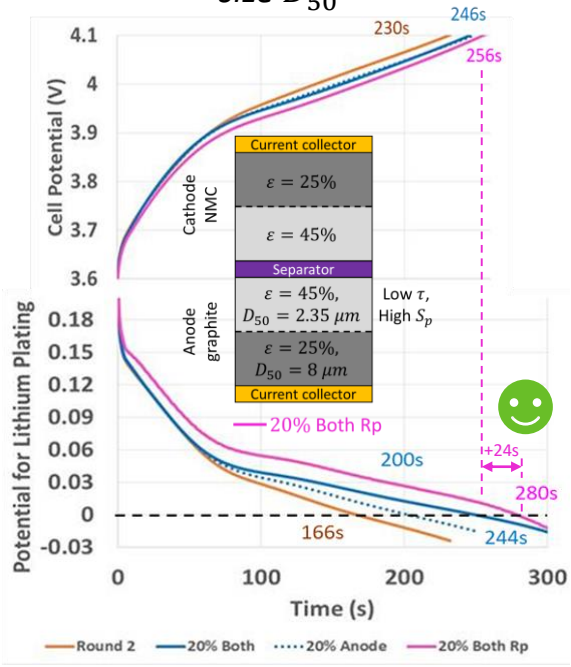
Models predict graded electrode porosity and particle size delay lithium plating

- Larger lithium plating delay when both electrodes have a bilayer architecture
  - Most gains are achieved with a 20% porosity offset.
- Combining graded porosity (→locally reduce tortuosity) and particle size (→ locally increase specific surface area and lithiation uniformity) provides further improvement
  - Cut-off voltage reached 24s before plating condition @6C CC
- Optimal dual layer parameters to be determined

Graded porosity ε



Graded porosity ε and particle size D_{50}

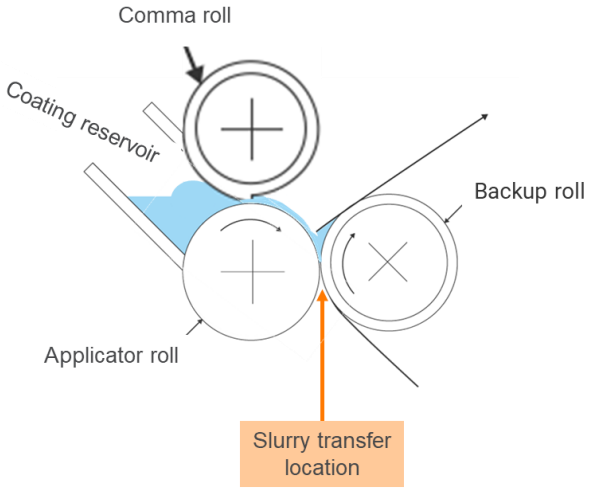


CAMP FACILITY EFFORTS TO MAKE BILAYERS WITH DUAL PARTICLES & POROSITY

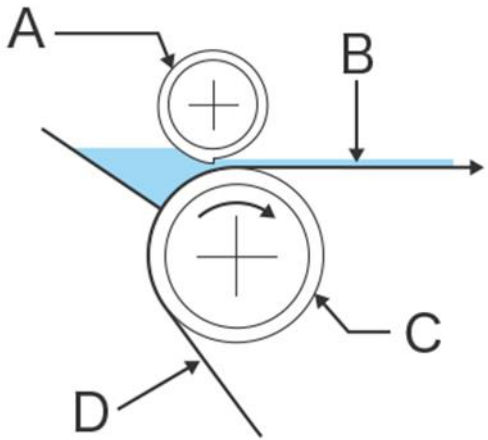
Two coating methods used: Reverse Comma (rc) and Knife-over-roll (kor) with and without NMP pre-wetting

Nearly all CAMP Facility electrodes have been coated using this preferred method.

Reverse comma



Knife-over-roll



A. Comma Bar
B. Coating
C. Backup roll
D. Substrate (web)

This method is not preferred due to the lack of intermittent coating capabilities. However, it does minimize "craters" due to air pockets bursting, specifically when performing dual layer coatings.

Modified images from:
https://www.keyence.com/ss/products/measure/sealing/coater-type/roll.jsp

Purchasing Slot-die Coater for more capabilities

NUMEROUS BILAYER ANODES FABRICATED

All Electrodes were Screened in Coin Cells under 6C Charge Cycles

- Graphite particles used: SLC1506T (baseline), SLC1520P, MCMB, and blends of each
- Cu:Large:Small and Cu:Small:Large

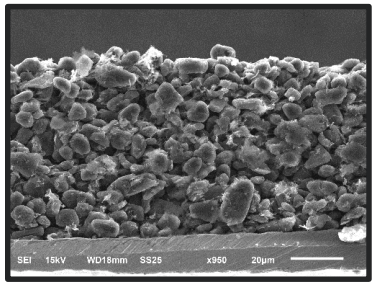
- Coin cell sets of each were made versus NMC532 and cycled at 30°C to:
  - Formation only,
  - 10, 25, and 50 cycles at 6C
- Cells were opened and anodes rinsed and photographed

Formation
1Hr C/10 Tap Charge, 5 Hr OCV
3.0-4.1V: C/10 Cycles - 3x
C/2 Cycles - 3x

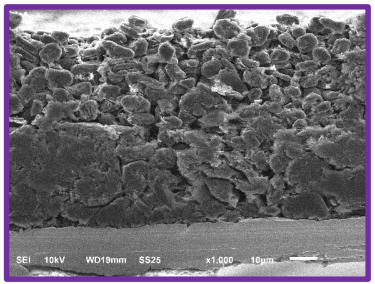
Fast Cycling
10, 25, & 50 Cycles of
6C Charge, C/2 Discharge

POST TEST OF 6C CYCLED ANODES REVEALED LARGE GRAPHITE LEAD TO Li PLATING

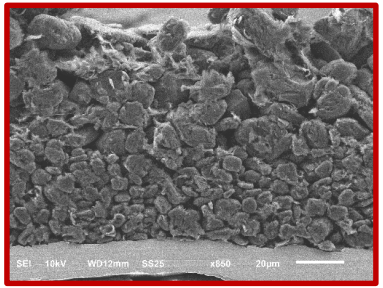
Large Graphite Led to Li Plating (probably due to lower surface area)



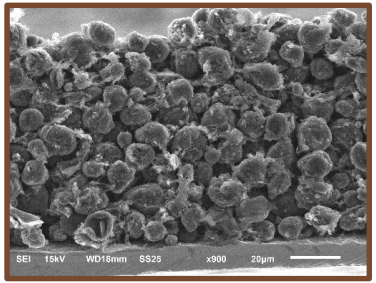
#0 – SLC 1506T



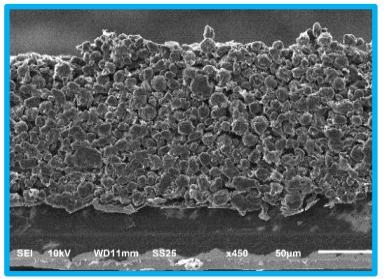
#2 – Cu : SLC 1520P : 1506T



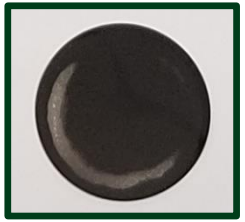
#5 – Cu : SLC 1506T : 1520P

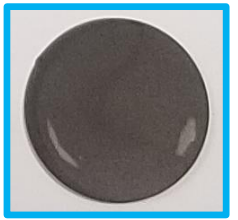


#10 - MCMB



#11 - SLC 1506T/MCMB Mix





- Electrodes with dual porosity layers were fabricated, but testing was interrupted due to COVID-19

❖ **Cross-Sections are from Pristine Electrodes**
❖ **Coin cell electrode photos are post cycling (after 50 fast charge cycles)**

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RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

New Thrust Area - Comments below based on Review of BAT339

- *Addressing inhomogeneity in graphite electrodes via operando experiments is outstanding. The reviewer wondered whether this set of experiment can be done in positive electrodes.*
  - Yes, plans are ongoing to develop bilayer cathodes based on modeling predictions.
- *It would be valuable if the binder content could be greatly reduced in the electrodes as it likely contributes directly to the electrode impedance.*
  - Agreed, the binder (and carbon) content were kept high in the hopes that better layer-to-layer adhesion would occur (and because it was a standard composition for CAMP Facility. Future plans will increase active material closer to 97%.
- *Small amounts of silicon oxide or an advanced silicon material (less than 10 wt%) could play an important role in simultaneously achieving energy density and fast charge goals.*
  - CAMP Facility is also very active in Silicon Deep Dive, and will eventually try incorporating Si-based materials. At this time, graphite-only was used to simplify modeling and analysis.

COLLABORATION ACROSS LABS AND UNIVERSITIES

- Five national laboratories (Argonne, NREL, INL, SLAC, and LBNL) and three universities (Stanford, UC-Berkeley, and Princeton) have teamed to form this integrated effort focused on enabling fast charge capability.
- National User Facilities involved in this work presented include the Advanced Photon Source. International Facilities include the European Synchrotron Radiation Facility.
- This effort is part of a broad range of unified studies (BAT386, BAT456, BAT457, BAT458, BAT459, BAT460, BAT461, BAT462,BAT463, BAT471).

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REMAINING CHALLENGES AND BARRIERS

- While the freeze-tape cast method is able to make an electrode with the lowest tortuosity, it may be difficult to densify the primary region required in an ideal secondary pore network

PROPOSED FUTURE RESEARCH

- Develop bilayer cathodes with differing porosity as predicted by model
  - May also vary particle size in each layer
- Continue to develop bilayer anodes, but with smaller graphite particles near separator – obtaining source of smaller graphite
  - Reduce the amount of binder and carbon additives to increase energy density
- Try incorporating pore formers (salt, volatile solids, etc.) to create secondary pores
  - Continue discussion and experiments with Univ. Michigan on laser ablation

Any proposed future work is subject to change based on funding levels.

SUMMARY

- Developed model to design two electrode architectures that reduce lithium plating
- Predicted that secondary pore network (SPN) architecture has a combined positive through-plane and negative in-plane diffusion impact
  - Electrode microstructure matrix must be densified to keep constant the gravimetric- and volumetric-specific theoretical capacities at constant electrode thickness
  - Poor in-plane diffusion eventually limits the SPN volume ratio
- Predicted that bilayer architectures can reduce lithium plating
  - Bilayer cathode is as important as bilayer anode
  - Smaller graphite particles are needed near separator
  - Binder and conductive additive content needs to be reduced
- Fabricated electrodes via freeze-tape cast to mimic SPN
  - Need to lower porosity
- Fabricated bilayer anodes to validate model prediction
  - Low surface area of extra large graphite particles led to Li plating

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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XCEL eXtreme Fast Charge Cell Evaluation of Lithium-Ion Batteries
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

TECHNICAL BACK-UP SLIDES

BASELINE ELECTRODES USED IN 2019-2020

Referred to as “Round 2” (3 mAh/cm² anode loading)

Anode: LN3107-190-4A

91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid

Lot#: 573-824, received 03/11/2016
Single-sided coating, CFF-B36 anode

Cu Foil Thickness: 10 µm
Total Electrode Thickness: 80 µm
Total Coating Thickness: 70 µm
Porosity: 34.5 %
Total SS Coating Loading: 9.94 mg/cm^2
Total SS Coating Density: 1.42 g/cm^3

Made by CAMP Facility

Cathode: LN3107-189-3

90 wt% Toda NMC532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

Matched for 4.1V full cell cycling
Prod:NCM-04ST, Lot#:7720301
Single-sided coating, CFF-B36 cathode

Al Foil Thickness: 20 µm
Al Foil Loading: 5.39 mg/cm^2
Total Electrode Thickness: 91 µm
Coating Thickness: 71 µm
Porosity: 35.4 %
Total Coating Loading: 18.63 mg/cm^2
Total Coating Density: 2.62 g/cm^3

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